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Synthesis of Oligo(α-D-glycosyl phosphate) Derivatives by a Phosphoramidite Method via Boranophosphate Intermediates

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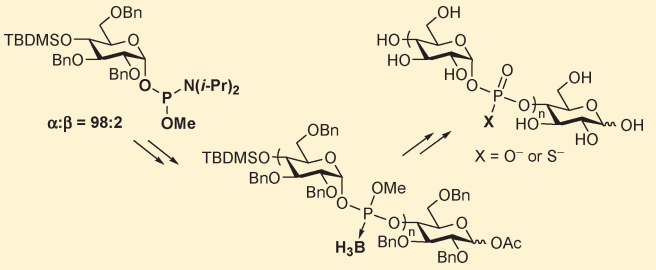
Supporting Information

ABSTRACT: An efficient method for the synthesis of short oligo(α-D-glycosyl boranophosphate) derivatives by using an α-D-glycosyl phosphoramidite as a monomer unit was developed. The synthesis of oligomers was carried out by repeating a cycle consisting of the condensation of the monomer unit with a terminal hydroxy group of carbohydrates, boronation of the resultant phosphite intermediates, and terminal deprotection. The phosphoramidite monomer unit was synthesized from the corresponding glycosyl iodide and methyl *N,N*-diisopropylphosphonamidate in a highly α-selective manner. Di- and tri(α-D-glycosyl boranophosphate) derivatives obtained by the synthetic cycle were converted into the corresponding *H*-phosphonate diester derivatives, which were then used to synthesize di- and tri(α-D-glycosyl phosphate) derivatives including a fragment of *Leishmania* glycocalyx lipophosphoglycans.



INTRODUCTION

Natural phosphoglycans containing glycosyl phosphate units are found in the cell wall or capsule of bacteria and the glycocalyx of protozoan parasites, such as *Neisseria meningitidis*, *Streptococcus pneumoniae*, and *Leishmania*, and work as antigenic determinants.[1,2] Therefore, structural and functional studies of these biomolecules are important to develop therapeutics against these pathogenic organisms.[1,2] Since chemically synthesized phosphoglycans and their analogues are quite useful for these studies, a variety of studies have been conducted to develop an efficient method to synthesize glycosyl phosphate derivatives and phosphoglycans.[3] Currently, these molecules, particularly those containing multiple glycosyl phosphate units, are usually synthesized by the *H*-phosphonate method.[2a,3−6] For example, phosphoglycans containing two to four glycosyl phosphate repeating units have been synthesized by this method.[2a,3−5] However, it has been reported that the synthesis of phosphoglycans containing more glycosyl phosphate units is still difficult.[5] It may be due to the instability of glycosyl *H*-phosphonodiester intermediates and/or the existence of polar and nucleophilic P−O$^-$ groups of glycosyl phosphodiester intermediates, which may cause some side reactions or difficulty in chromatographic purification.

With this background, we have sought to develop an efficient method to synthesize phosphoglycans by a different approach and focused on glycosyl phosphoramidites[4a,7a,8] and borano phosphates.[4d,7b,7c,9] Phosphoramidites are by far the most frequently used compounds to synthesize phosphate-containing biomolecules, especially oligonucleotides (phosphoramidite method).[10] In contrast, the phosphoramidite method has been scarcely used to synthesize phosphoglycans. Only a few studies on the synthesis of disaccharide phosphates have been reported to date,[4a,8] and the synthesis of more complex molecules has not been achieved. It is attributed to the following reasons: (1) a versatile method to synthesize diastereopure α- or β-glycosyl phosphoramidites has not been developed, and (2) glycosyl phosphite and phosphate triester intermediates, which are generated by condensation of the glycosyl phosphoramidites with other saccharides and subsequent oxidation, are prone to decomposition by acid activators (e.g., 1*H*-tetrazole), neighboring group participation, and/or during chromatographic purification.[3,11]

Very recently, we have developed a method to synthesize glycosyl phosphites and phosphoramidites in a highly α-selective manner.[7a] This method would solve the first problem in applying the phosphoramidite method to the synthesis of phosphoglycans. It should be noted that most of the phosphoglycans in nature consist of α-glycosyl phosphates.[3] We have also found that glycosyl phosphite triester intermediates can be temporarily protected by boronation of the phosphorus atom instead of oxidation and that the resultant glycosyl boranophosphate triesters can be converted into the corresponding glycosyl phosphate diesters as well as some other *P*-modified analogues, such as phosphorothioates.[7b,c,12] The boranophosphate intermediates are chemically stable under various reaction conditions for the synthesis of phosphoglycans, and the new strategy utilizing boranophosphates would solve the second problem. In this paper, we report the development of an efficient method to synthesize phosphoglycans by using an α-glycosyl phosphoramidite monomers and glycosyl

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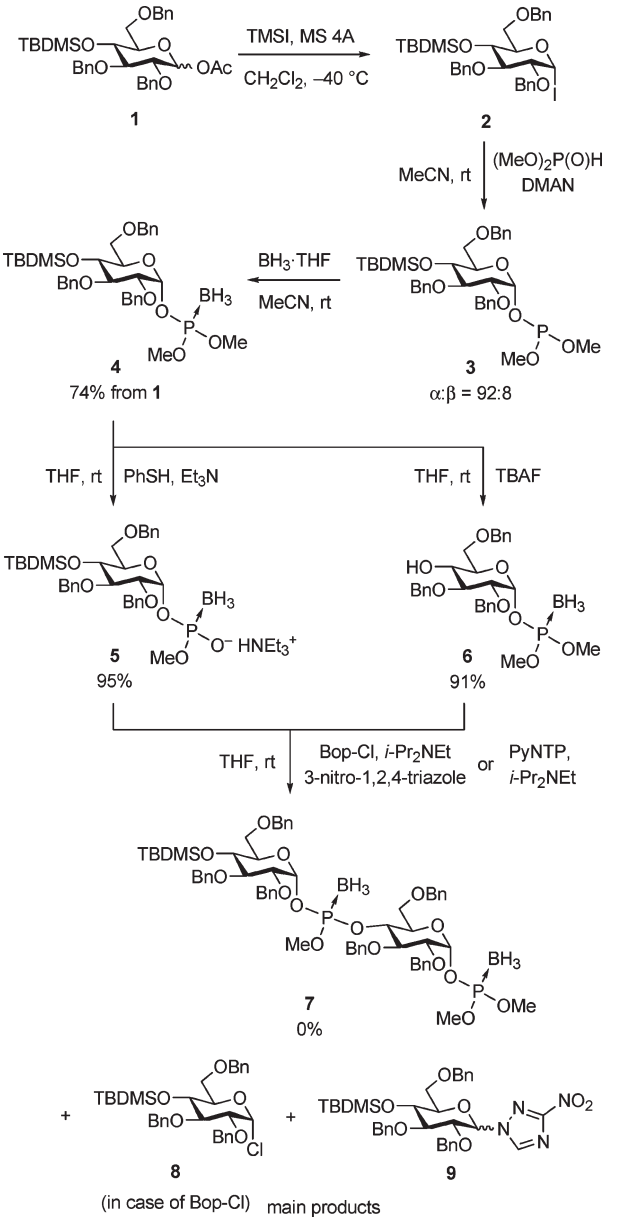
Scheme 1. Stereoselective Synthesis of α-D-Glucosyl Boranophosphate Derivatives 4−6 and an Attempt To Synthesize Boranophosphotriester-Linked Disaccharide 7 via Condensation Reaction

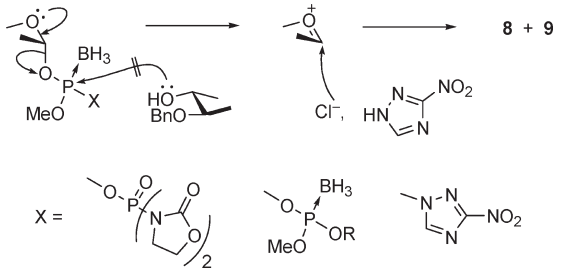


boranophosphate intermediates. An attempt to use glycosyl boranophosphates as monomers is also described.

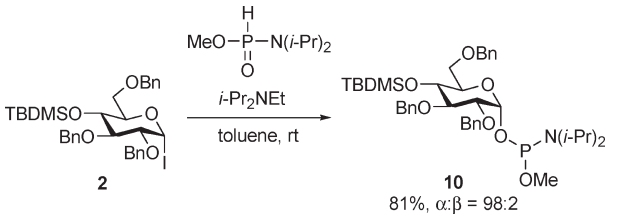
RESULTS AND DISCUSSION

First, we describe our attempt to synthesize disaccharide phosphate derivatives by using an α-glycosyl boranophosphate derivative as a monomer unit (Scheme 1). We have recently reported that a β-D-glucopyranosyl boranophosphate diester and an α-D-mannopyranosyl boranophosphate diester underwent smooth condensation reactions to give the corresponding disaccharide boranophosphates and some other glycosyl boranophosphate derivatives in excellent yields.[7b,c] The resultant boranophosphates can be converted into the corresponding

Scheme 2. Plausible Mechanism for Generation of 8 and 9



Scheme 3. Stereoselective Synthesis of α-D-Glucosyl Phosphoramidite 10



phosphate diesters. We have also reported that the reaction of glycosyl iodides with an *H*-phosphonate diester afforded glycosyl phosphites in a highly α-selective manner.[7a] The glycosyl phosphites can be converted into the boranophosphate derivatives by *P*-boronation. By combining these methods, we tried to synthesize an α-boranophosphotriester-linked disaccharide.

As shown in Scheme 1, dimethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranosyl boranophosphate **4** was synthesized by using a glycosyl iodide **2**, dimethyl *H*-phosphonate, and 1,8-bis(dimethylamino)naphthalene (DMAN) according to our recent procedure.[7a] The α-isomer was obtained α-selectively (α:β = 92:8). One of the two methyl groups of **4** was then removed by treatment with PhSH and triethylamine to give methyl 2,3,6-tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranosyl boranophosphate diester **5**. The TBDMS group of **4** was also removed by treatment with tetrabutylammonium fluoride (TBAF) to give dimethyl 2,3,6-tri-*O*-Bn-α-D-glucopyranosyl boranophosphate **6**. Then, we attempted to condense these two building blocks (**5**, **6**) under the same conditions as we used to synthesize β-D-glucopyranosyl boranophosphate derivatives with bis(2-oxo-3-oxazolidinyl)phosphinic chloride (Bop-Cl) as a condensing reagent, 3-nitro-1,2,4-triazole (NT) as a nucleophilic catalyst, and *i*-Pr$_2$NEt (boranophosphotriester method).[7b] However, the desired boranophosphotriester-linked disaccharide **7** was not obtained, but the formation of a glucosyl chloride **8** and a glucosyl nitrotriazolide **9** was observed by ^{1}H NMR and MALDI-TOF MS. The use of 3-nitro-1,2,4-triazol-1-yl-tris(pyrrolidin-1-yl)phosphonium hexafluorophosphate (PyNTP) as a condensing reagent[7c] gave a similar result. All the attempts to improve the result by changing the reaction conditions resulted in failure. The results were completely opposite from those previously obtained with β-D-glucopyranosyl boranophosphate derivatives,[7b,c] indicating that the anomeric configuration and/or the protecting groups of substrates were important factors in the boranophosphotriester method. Although the detailed reaction mechanism is not clear yet, the formation of the byproducts **8** and **9** indicates that an

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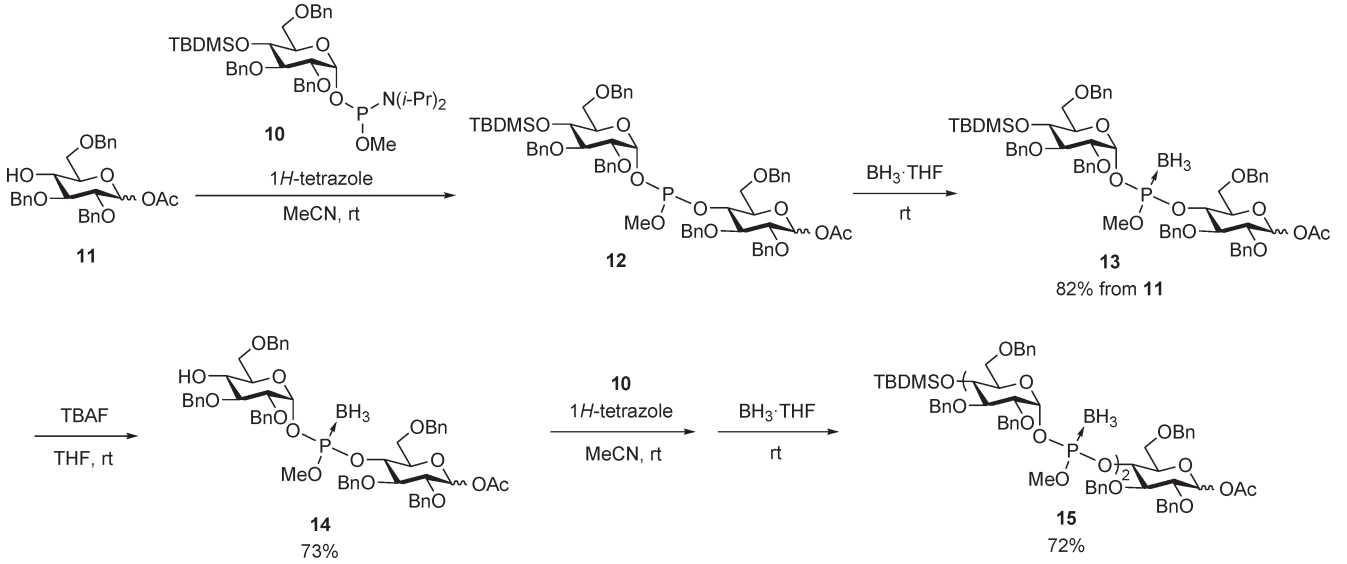
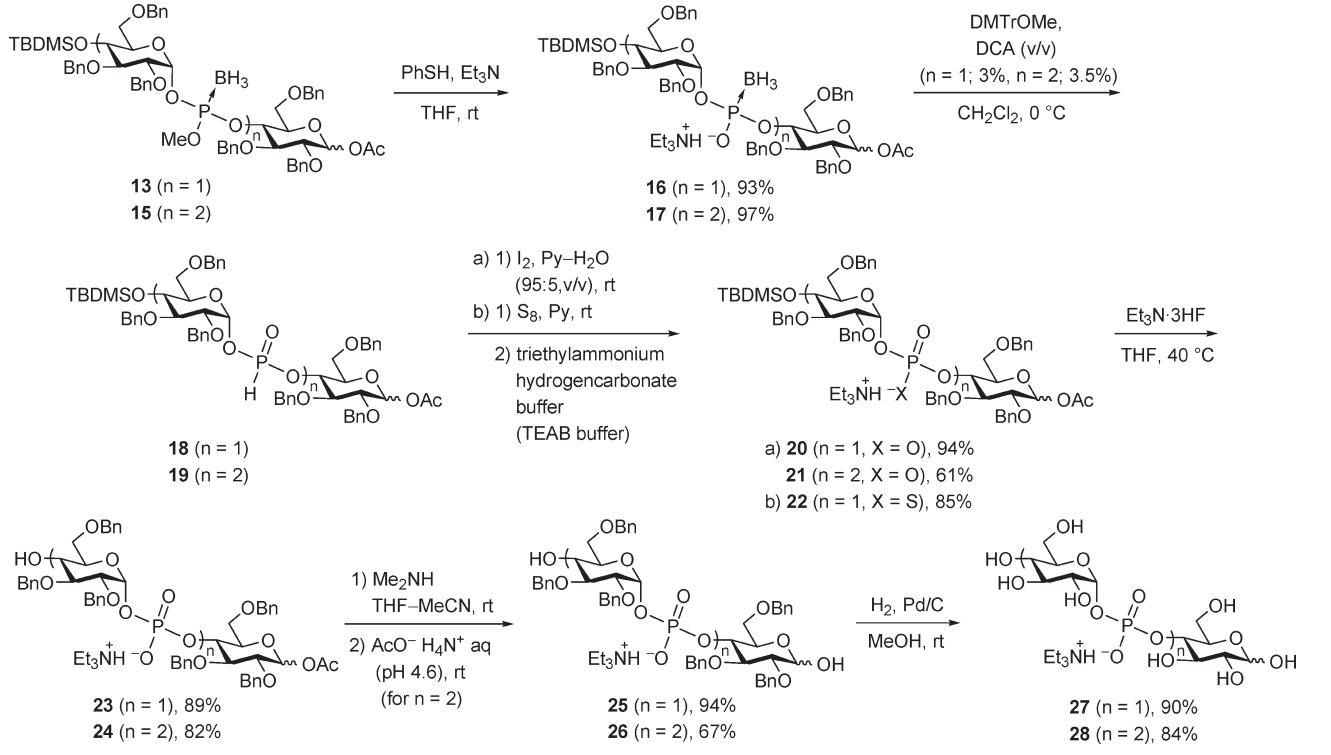
Scheme 4. Synthesis of Oligo(α-D-glucosyl boranophosphate) Derivatives by the Phosphoramidite Method



Scheme 5. Synthesis of Oligo(α-D-glucosyl phosphate) Derivatives from Boranophosphate Counterparts



oxocarbenium ion may be generated[13] by the elimination of the activated boranophosphate moiety (Scheme 2). The active intermediates generated from **5** must be less reactive to the hydroxy group of **6** than the β-isomeric counterparts due to the steric hindrance of the glucopyranose moiety. The 4-*O*-TBDMS group may also increase the steric hindrance. Furthermore, the oxocarbenium ion is generated more easily in the case of per-*O*-Bn glycosyl phosphate derivatives compared to their per-*O*-acyl counterparts,[13] which we successfully used in the boranophosphotriester method before.[7b,c] We speculate that the results shown in Scheme 1 reflect the combined effect of these factors.

Given these results, we turned our attention to the phosphoramidite method to synthesize α-glycosyl boranophosphotriester-linked phosphoglycans. The requisite α-glycosyl phosphoramidite monomer **10** can be synthesized by the same α-selective phosphitylation of the glucosyl iodide **2** (Scheme 3).[7a] The reaction was also almost completely α-selective (α:β = 98:2). Condensation of **10** with a glucose derivative **11** was performed

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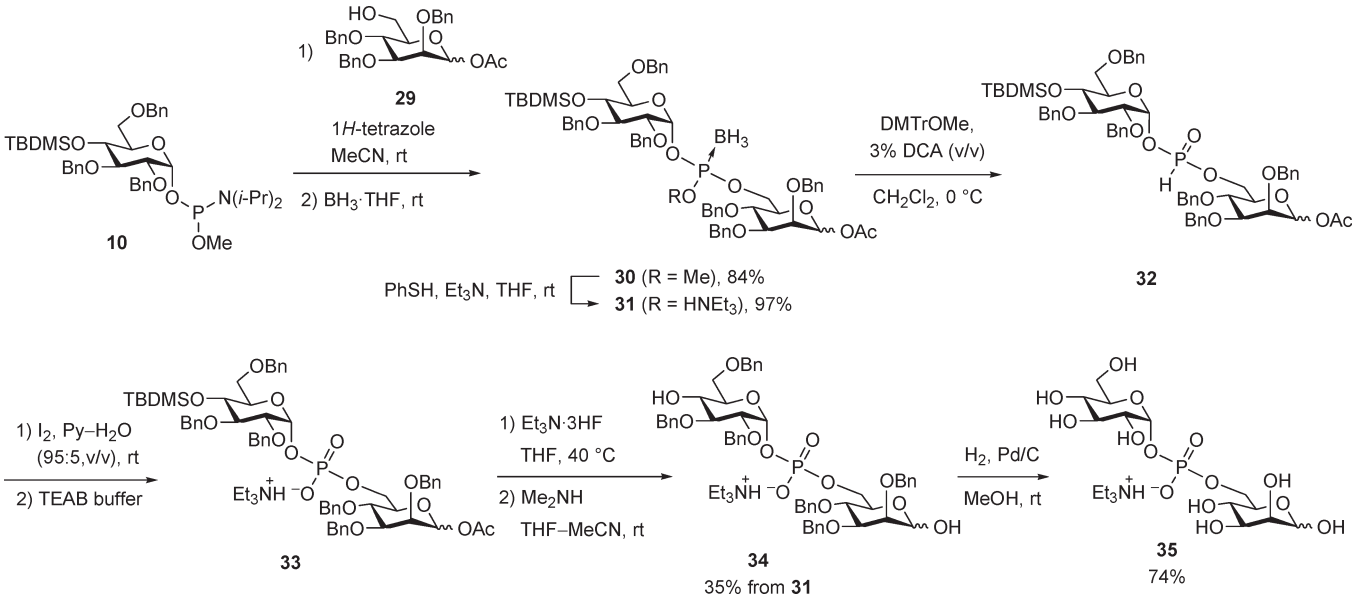
Scheme 6. Synthesis of α-D-Glc-(1-*P*-6)-D-Man 35 by the Phosphoramidite Method



in the presence of 1*H*-tetrazole as an activating agent (Scheme 4). The reaction was completed within 25 min at rt. Subsequently, the phosphite intermediate **12** was in situ boronated by treatment with BH_3·THF. A ^{31}P NMR analysis showed that these reactions proceeded without any observable side reactions. The desired disaccharide boranophosphate **13** was isolated in good yield.

For a stepwise synthesis of a phosphoglycan chain, a terminal protecting group must be selectively removed. In the case of **13**, the 4-*O*-TBDMS group was selectively removed to give **14**, which was then coupled with the phosphoramidite monomer **10** again. Subsequent *P*-boronation of the phosphite intermediate gave the boranophosphotriester-linked trisaccharide **15**. Thus, we demonstrated that the phosphoramidite method was applicable to a stepwise chain elongation of oligo(α-glycosyl boranophosphate) derivatives.

Next, we attempted to convert the boranophosphotriester-linked disaccharide **13** and trisaccharide **15** into the phosphodiester-linked counterparts according to the method we recently developed (Scheme 5).[7b,c] First, the methyl group on the boranophosphotriester of **13** and **15** was removed by treatment with PhSH and Et_3N to give the boranophosphodiesters **16** and **17**. The compounds **16** and **17** were then treated with 4,4′-dimethoxytrityl (DMTr) cation generated in situ from DMTrOMe and dichloroacetic acid (DCA) to convert the boranophosphodiester-linked disaccharides into the *H*-phosphonodiester-linked **18** and **19**. A ^{31}P NMR analysis showed that the conversion was virtually quantitative. The use of trityl (Tr) cation generated from TrOMe gave the same results. The resultant *H*-phosphonate diesters were oxidized in situ with I_2−H_2O−pyridine (Py) to give the desired phosphodiester-linked disaccharide **20** and trisaccharide **21**. In addition, thiophosphodiester-linked disaccharide **22** was synthesized by the sulfurization of **18**. The TBDMS groups of **20** and **21** were removed by treatment with Et_3N·3HF at 40 °C to give **23** and **24**. The anomeric acetyl group of the disaccharide **23** was successfully removed by treatment with Me_2NH to give **25** in excellent yield. In contrast, the treatment of **24** with Me_2NH afforded a mixture of the desired **26** and an *N*,*N*-dimethylaminoglycoside [analyzed by ^1H NMR, ^{13}C NMR, and MALDI-TOF MS (calcd for $C_{83}H_{91}NO_{21}P_2Na$ $[M - 2H + Na]^-$ 1522.5462, found 1522.5399)], though the aminoglycoside was easily hydrolyzed by treatment with ammonium acetate buffer (pH 4.6) to give the desired product **26**.[14] All the Bn groups were then removed by catalytic hydrogenolysis to give the desired phosphodiester-linked fully deprotected disaccharide **27** and trisaccharide **28**.

Finally, we applied the method to the synthesis of α-D-Glc-(1-*P*-6)-D-Man **35**, a fragment of *Leishmania* glycocalyx lipophosphoglycans (Scheme 6).[2b,3] The synthesis of the boranophosphotriester-linked disaccharide **30** by condensation of the phosphoramidite **10**, subsequent conversion to the phosphodiester-linked disaccharide **33** via the *H*-phosphonate diester intermediate **32**, and deprotection was performed according to the same procedure without significant side reactions to give **35** in good total yield.

CONCLUSION

In conclusion, the present study showed that the phosphoramidite method can be applicable to the synthesis of short oligo(α-glycosyl phosphate) derivatives via the boranophosphate intermediates. To the best of our knowledge, this is the first report on the synthesis of oligo(glycosyl phosphate) derivatives longer than disaccharide phosphates by using the phosphoramidite method. The high efficiency of the chain elongation by this method owing to the reactivity of the phosphoramidite monomers would be advantageous for the synthesis of biomolecules consisting of multiple glycosyl phosphate units.

EXPERIMENTAL SECTION

2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-D-glucopyranosyl Acetate (1). 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranose[15] (8.20 g, 14.5 mmol) was dried by repeated coevaporation with dry Py and dissolved in dry Py (29.5 mL) under Ar. Acetic anhydride (2.80 mL, 29.6 mmol) was added to the solution at 0 °C and the mixture was allowed to stir for 19 h at rt. A saturated $NaHCO_3$ aqueous solution (30 mL) and AcOEt (30 mL) were then added successively to the mixture. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solutions (2 × 50 mL),

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dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (5:2, v/v) as an eluent to give **1** as a colorless oil (8.00 g, 13.2 mmol, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.18 (m, 15H, CH_2Ph), 6.43 (d, J = 3.0 Hz, α-H-1), 5.71 (d, J = 8.0 Hz, β-H-1), 5.11−4.49 (m, 6H, CH_2Ph), 3.87−3.51 (m, 6H, H-2, H-3, H-4, H-5, H-6), 2.17 (s, α-OCOCH_3), 2.04 (s, β-OCOCH_3), 0.87−0.82 (m, 9H, SiC(CH_3)$_3$), 0.05−0.02 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 169.1 (OCOCH_3), 138.9, 138.6, 138.1, 138.0, 137.9, 137.3 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 126.8 (CH, Ar), 93.9 (β-C-1), 89.6 (α-C-1), 84.6 (CH), 81.5 (CH), 81.0 (CH), 79.4 (CH), 77.2 (CH), 76.9 (CH), 74.7 (CH_2Ph), 74.7 (CH_2Ph), 74.6 (CH_2Ph), 74.2 (CH), 73.2 (CH_2Ph), 73.1 (CH_2Ph), 72.9 (CH_2Ph), 70.2 (CH), 69.9 (CH), 68.5 (C-6), 25.9, 25.8 (SiC(CH_3)$_3$), 21.1, 21.0 (OCOCH_3), 18.0, 17.9 (SiC(CH_3)$_3$), −3.86, −3.90, −5.00, −5.10 (Si(CH_3)$_2$). HRMS (ESI): calcd for $C_{35}H_{46}O_7SiK$ $[M + K]^+$ 645.2644, found 645.2647.

Dimethyl 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranosyl Boranophosphate (4). 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-D-glucopyranosyl acetate **1** (0.975 g, 1.6 mmol) was dried by repeated coevaporation with dry Py and dry toluene and dissolved in dry CH_2Cl_2 (32.5 mL). MS 4A (4A molecular sieves) were added to the mixture. Trimethylsilyl iodide (0.260 mL, 1.8 mmol) was added to the solution at −40 °C with stirring. Additional trimethylsilyl iodide (92.5 μL, 0.65 mmol) was added after 3 h and again added (70 μL, 0.37 mmol) after 1 h. The mixture was then allowed to stir for 1 h at the same temperature. The mixture was then coevaporated with dry toluene (8 × 16 mL) at 0 °C to remove any volatiles. A solution of dimethyl *H*-phosphonate (1.50 mL, 16.3 mmol) and DMAN (0.691 g, 4.0 mmol) in dry MeCN (16.1 mL), which was dried over MS 3A (3A molecular sieves) prior to use, was added to the residue at rt, and the mixture was stirred for 1 d. A saturated $NaHCO_3$ aqueous solution (20 mL) and $CHCl_3$ (20 mL) were then added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then dissolved in dry MeCN (16.5 mL) and a 1 M solution of BH_3·THF in THF (16.5 mL, 16.5 mmol) was added to the solution at rt. After stirring for 1 h, a saturated $NaHCO_3$ aqueous solution (20 mL) and $CHCl_3$ (20 mL) were added successively. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solutions (2 × 20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (5:2, v/v) as an eluent to give **4** as a brown oil (0.801 g, 1.2 mmol, 74%, α:β = 92:8). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33−7.22 (m, 15H, CH_2Ph), 5.85 (dd, J_{HH} = 3.0 Hz, J_{PH} = 7.7 Hz, α-H-1), 5.06−4.47 (m, 6H, CH_2Ph), 3.92−3.58 (m, 12H, H-2, H-3, H-4, H-5, H-6, POCH_3), 0.84−0.81 (m, 9H, SiC(CH_3)$_3$), 0.02 to −0.03 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.8, 138.0, 137.3 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 127.0 (CH, Ar), 94.3 (C-1), 80.6 (CH), 79.8 (CH), 79.7 (CH), 74.8 (CH_2Ph), 73.8 (CH), 73.3 (CH_2Ph), 73.0 (CH_2Ph), 70.1 (CH), 68.6 (C-6), 53.5, 53.4, (POCH_3), 25.9 (SiC(CH_3)$_3$), 18.1 (SiC(CH_3)$_3$), −3.78, −4.98 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 119.0−115.6 (m). HRMS (ESI): calcd for $C_{35}H_{52}BO_8PSiNa$ $[M + Na]^+$ 693.3154, found 693.3155.

Methyl 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranosyl Boranophosphate Triethylammonium Salt (5). Triethylamine (1.15 mL, 8.3 mmol) and benzenethiol (0.850 mL, 8.2 mmol) were added successively to a solution of dimethyl 2,3,6-tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranosyl boranophosphate **4** (137 mg, 0.20 mmol) in dry THF (2.0 mL). Additional triethylamine (0.55 mL, 4.0 mmol) and benzenethiol (0.42 mL, 4.1 mmol) were added after 14 h, and after 5 h more triethylamine (0.55 mL, 4.0 mmol) and benzenethiol (0.42 mL, 4.1 mmol) were added. The mixture was then allowed to stir for 6 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and $CHCl_3$ (5.0 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (5.0 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (98:1:1−97:1:2, v/v/v) as an eluent. The fractions containing **5** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give **5** as a yellow oil (146 mg, 0.19 mmol, 95%, α:β = 97:3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35−7.18 (m, 15H, CH_2Ph), 5.93 (td, J_{HH} = 3.3 Hz, J_{PH} = 8.5 Hz, H-1), 5.09−4.47 (m, 6H, CH_2Ph), 4.07−3.55 (m, 9H, H-2, H-3, H-4, H-5, H-6, POCH_3), 2.96−2.87 (q, 6H, NCH_2CH$_3$), 1.20 (t, 9H, NCH$_2$CH_3) 0.87−0.78 (m, 9H, SiC(CH_3)$_3$), 0.01 to −0.03 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.3, 139.2, 138.4, 138.3, 138.2 (C, Ar), 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8 (CH, Ar), 91.1, 91.0, 90.7, 90.6 (C-1), 80.9 (CH), 80.7 (CH), 80.6 (CH), 80.5 (CH), 80.4 (CH), 77.2 (CH), 74.5 (CH_2Ph), 74.4 (CH_2Ph), 73.1 (CH_2Ph), 73.0 (CH_2Ph), 72.4 (CH), 72.3 (CH), 72.2 (CH_2Ph), 71.7 (CH_2Ph), 70.5 (CH), 70.4 (CH), 69.1 (C-6), 68.9 (C-6), 51.1, 51.0, 50.7, 50.6 (POCH_3), 45.1 (NCH_2CH$_3$), 25.9 (SiC(CH_3)$_3$), 18.1, 18.0 (SiC(CH_3)$_3$), 8.36 (NCH_2CH$_3$), −3.75, −3.79, −5.02, −5.03 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 100.2−94.6 (m). HRMS (ESI): calcd for $C_{34}H_{50}BO_8PSiNa$ $[M + Na]^+$ 679.2998, found 679.3022.

Dimethyl 2,3,6-Tri-*O*-Bn-α-D-glucopyranosyl Boranophosphate (6). Dimethyl 2,3,6-tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranosyl boranophosphate **4** (0.133 g, 0.20 mmol), which was dried by repeated coevaporation with dry toluene, was added to dry THF (1.6 mL). A 1 M solution of TBAF in THF (0.40 mL, 0.40 mmol), which was dried over MS 3A prior to use, was added to the solution at rt. The mixture was allowed to stir for 30 min at rt. Then a saturated $NaHCO_3$ aqueous solution (3.0 mL) and $CHCl_3$ (5.0 mL) were added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 5.0 mL). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (2:1, v/v) as an eluent to give **6** as a colorless oil (0.102 g, 0.182 mmol, 91%, α:β = 96:4). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38−7.24 (m, 15H, CH_2Ph), 5.82 (dd, J_{HH} = 3.3 Hz, J_{PH} = 7.7 Hz, α-H-1), 5.00−4.50 (m, 6H, CH_2Ph), 3.95−3.57 (m, 12H, H-2, H-3, H-4, H-5, H-6, POCH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.4, 137.7, 137.4 (C, Ar), 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6 (CH, Ar), 94.5 (C-1), 80.3 (CH), 78.7 (CH), 78.6 (CH), 75.3 (CH_2Ph), 73.5 (CH_2Ph), 72.9 (CH_2Ph), 72.1 (CH), 70.1 (CH), 69.1 (C-6), 53.5, 53.4, 53.3 (POCH_3). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 121.4−117.6 (m). HRMS (ESI): calcd for $C_{29}H_{38}BO_8PK$ $[M + K]^+$ 595.2029, found 595.2041.

Methyl 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-α-D-glucopyranosyl *N*,*N*-diisopropylphosphoramidite (10). 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-D-glucopyranosyl acetate **1** (2.33 g, 3.8 mmol) was dried by repeated coevaporation with dry Py and dry toluene and dissolved in dry CH_2Cl_2 (32.5 mL). MS 4A were added to the solution. The solution was cooled to −15 °C and trimethylsilyl iodide (0.650 mL, 4.6 mmol) was added. The mixture was then allowed to stir for 2 h at 0 °C and additional trimethylsilyl iodide (54.0 μL, 0.365 mmol) was added. After 20 min, the mixture was coevaporated with dry toluene (5 × 30 mL) at 0 °C. A solution of methyl *N*,*N*-diisopropylphosphonamidate (6.94 g, 38.8 mmol) and diisopropylethylamine (1.35 mL, 9.5 mmol) in dry toluene (38 mL), which was dried over MS 4A prior to use, was added to the

residue at rt. After 1 d, the mixture was filtered, and a saturated $NaHCO_3$ aqueous solution (40 mL) and AcOEt (40 mL) were added successively to the filtrate. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solutions (2 × 30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by NH silica gel (Fuji Silysia Chemical, Inc. DM1020 100−200 mesh) column chromatography using hexane−AcOEt (10:1, v/v) as an eluent to give **10** as a colorless oil (2.24 g, 3.1 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35−7.18 (m, 15H, CH_2Ph), 5.49−5.45 (m, 1H, α-H-1), 5.08−4.47 (m, 6H, CH_2Ph), 3.98−3.55 (m, 8H, H-2, H-3, H-4, H-5, H-6, NCH(CH_3)$_2$), 3.47, 3.43, 3.38 (s, 3H, POCH_3), 1.26−1.12 (m, 12H, NCH(CH_3)$_2$), 0.87−0.81 (m, 9H, SiC(CH_3)$_3$), 0.03 to −0.04 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.2, 139.1, 138.3, 138.2, 138.1, 138.0 (C, Ar), 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9 (CH, Ar), 92.7, 92.4, 91.9, 91.6 (C-1), 81.3 (CH), 81.1 (CH), 81.0 (CH), 80.9 (CH), 80.6 (CH), 80.5 (CH), 77.2 (CH), 74.6 (CH_2Ph), 73.1 (CH_2Ph), 73.0 (CH_2Ph), 72.4 (CH), 72.2 (CH, CH_2Ph), 70.6 (CH), 70.2 (CH), 68.9 (C-6), 68.5 (C-6), 51.1, 50.9, 50.7, 50.5 (POCH_3), 43.5, 43.3, 43.2, 43.0 (NCH(CH_3)$_2$), 25.9 (SiC(CH_3)$_3$), 24.8, 24.7, 24.6, 24.5, 24.4, 24.3 (NCH(CH_3)$_2$), 18.0 (SiC(CH_3)$_3$), −3.78, −4.98, −5.06 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 152.6, 149.8 (s). HRMS (ESI): calcd for $C_{40}H_{60}NO_7PSiK$ $[M + K]^+$ 764.3508, found 764.3539.

2,3,6-Tri-*O*-Bn-D-glucopyranosyl Acetate (11). 2,3,6-Tri-*O*-Bn-4-*O*-TBDMS-D-glucopyranosyl acetate **1** (1.21 g, 2.0 mmol) was dried by repeated coevaporation with dry Py and dry toluene and dissolved in dry THF (20 mL) under Ar. A 1 M solution of TBAF in THF (3.00 mL, 3.0 mmol), which was dried over MS 3A prior to use, was added to the solution at rt, and the mixture was allowed to stir for 15 min. A saturated $NaHCO_3$ aqueous solution (20 mL) and AcOEt (20 mL) were then added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 50 mL). The aqueous layers were combined and back-extracted with AcOEt (2 × 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (5:2, v/v) as an eluent to give **11** as a colorless oil (0.804 g, 1.6 mmol, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33−7.16 (m, 15H, CH_2Ph), 6.36 (d, J = 3.6 Hz, α-H-1), 5.61 (d, J = 7.7 Hz, β-H-1), 4.97−4.45 (m, 6H, CH_2Ph), 3.86−3.48 (m, 6H, H-2, H-3, H-4, H-5, H-6), 2.10 (s, α-OCOCH_3), 1.99 (s, β-OCOCH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.0 (OCOCH$_3$), 138.4, 138.2, 137.9, 137.6, 137.5, 137.3 (C, Ar), 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (CH, Ar), 93.8 (β-C-1), 89.7 (α-C-1), 83.9 (CH), 80.7 (CH), 80.4 (CH), 78.2 (CH), 77.2 (CH), 75.1 (CH_2Ph), 74.7 (CH_2Ph), 74.6 (CH), 73.4 (CH_2Ph), 73.3 (CH_2Ph), 72.8 (CH_2Ph), 72.4 (CH), 70.7 (CH), 70.0 (CH), 69.1 (C-6), 69.0 (C-6), 20.9, 20.8 (OCOCH_3). HRMS (ESI): calcd for $C_{29}H_{32}O_7K$ $[M + K]^+$ 531.1780, found 531.1760.

Boranophosphotriester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (13). Compounds **10** (0.192 g, 0.26 mmol) and **11** (0.123 g, 0.25 mmol) were dried by repeated coevaporation with dry toluene and in vacuo overnight. A solution of 1*H*-tetrazole (35 mg, 0.50 mmol) in dry MeCN (2.5 mL), which was dried over MS 3A prior to use, was added to the mixture and the mixture was allowed to stir for 20 min at rt. A 1 M solution of BH_3·THF in THF (1.25 mL, 1.25 mmol) was then added, and the mixture was allowed to stir for 20 min at rt. A saturated $NaHCO_3$ aqueous solution (10 mL) and $CHCl_3$ (10 mL) were added successively to the mixture. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solutions (2 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (5:2, v/v) as an eluent to give **13** as a colorless foam (0.230 g, 0.20 mmol, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41−7.21 (m, 30H, CH_2Ph), 6.33, 6.30 (d, J = 3.6 Hz, α-H-1), 5.91−5.83 (m, 1H, α-H-1:CHOP), 5.58, 5.56 (d, J = 8.3 Hz, β-H-1), 4.98−4.77 (m, 3H, CH_2Ph), 4.70−3.45 (m, 24H, CH_2Ph, H-2, H-3, H-4, H-5, H-6, POCH_3), 2.14, 2.10, 2.03, 2.02 (s, 3H, OCOCH_3), 0.86−0.79 (m, 9H, SiC(CH_3)$_3$), 0.01 to −0.06 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.1 (OCOCH$_3$), 138.7, 138.6, 138.4, 138.2, 138.1, 138.0, 137.8, 137.3 (C, Ar), 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8 (CH, Ar), 94.9, 94.5 (C-1), 93.6 (β-COCOCH$_3$), 89.5 (α-COCOCH$_3$), 82.7 (CH), 80.8 (CH), 80.6 (CH), 79.8 (CH), 79.3 (CH), 78.8 (CH), 75.4, 75.2, 75.1, 74.9, 74.7, 74.6, 73.8, 73.5, 73.4, 73.3, 73.2, 73.1, 73.0, 72.8 (CH, CH_2), 70.1 (CH), 69.8 (CH), 68.5 (CH_2), 68.3 (CH_2), 68.1 (CH_2), 68.0 (CH_2), 54.1 (POCH$_3$), 25.9 (SiC(CH_3)$_3$), 21.0 (OCOCH$_3$), 18.0 (SiC(CH_3)$_3$), −3.85, −5.08 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 123.3−116.2 (m). HRMS (ESI): calcd for $C_{63}H_{80}BO_{14}PSiNa$ $[M + Na]^+$ 1153.5040, found 1153.5065.

Boranophosphotriester-Linked α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (14). Compound **13** (1.12 g, 0.99 mmol) was dried by repeated coevaporation with dry toluene and dissolved in dry THF (8.4 mL). A 1 M solution of TBAF in THF (2.0 mL, 2.0 mmol), which was dried over MS 3A prior to use, was then added at rt. The mixture was allowed to stir for 1.5 h at rt. A saturated $NaHCO_3$ aqueous solution (10 mL) and AcOEt (10 mL) were added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 20 mL). The aqueous layers were combined and back-extracted with AcOEt (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (3:1, v/v) as an eluent to give **14** as a colorless foam (0.738 g, 0.73 mmol, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35−7.21 (m, 30H, CH_2Ph), 6.32 (m, α-H-1), 5.83−5.80 (m, 1H, α-H-1:CHOP), 5.59−5.57 (m, β-H-1), 4.93−3.44 (m, 27H, H-2, H-3, H-4, H-5, H-6, CH_2Ph, POCH_3), 2.16, 2.13, 2.04, 2.03 (s, 3H, OCOCH_3), 1.15−0.11 (br, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.1 (OCOCH$_3$), 138.6, 138.4, 138.2, 137.7, 137.4, 137.3, 137.2 (C, Ar), 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.3, 127.2, 127.0, 126.9 (CH, Ar), 95.1, 94.8 (C-1), 93.6 (β-COCOCH$_3$), 89.4 (α-COCOCH$_3$), 82.7 (CH), 80.8 (CH), 80.3 (CH), 79.3 (CH), 78.6 (CH), 77.2 (CH), 75.5, 75.4, 75.3, 75.2, 75.0, 74.9, 74.7, 74.5 (CH, CH_2), 73.5 (CH_2), 73.4 (CH_2), 73.2 (CH_2), 73.0 (CH_2), 72.8 (CH), 72.4 (CH), 72.2 (CH), 71.9 (CH), 70.3 (CH), 70.2 (CH), 70.0 (CH), 68.9 (CH_2), 68.8 (CH_2), 68.3 (CH_2), 68.2 (CH_2), 68.0 (CH_2), 54.1 (POCH$_3$), 21.0 (OCOCH$_3$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 119.8−114.2 (m). HRMS (ESI): calcd for $C_{57}H_{66}BO_{14}PNa$ $[M + Na]^+$ 1039.4175, found 1039.4202.

Boranophosphotriester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (15). Compounds **10** (0.625 g, 0.86 mmol) and **14** (0.738 g, 0.73 mmol) were dried by repeated coevaporation with dry toluene and in vacuo overnight, and a solution of 1*H*-tetrazole (112 mg, 1.6 mmol) in dry MeCN (8.0 mL), which was dried over MS 3A prior to use, was added. The mixture was allowed to stir for 15 min at rt. A 1 M solution of BH_3·THF in THF (4.0 mL, 4.0 mmol) was then added to the mixture at rt. The mixture was allowed to stir for 20 min. A saturated $NaHCO_3$ aqueous solution (5.0 mL) and AcOEt (10 mL) were added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 10 mL). The aqueous layers were combined and back-extracted with AcOEt (2 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (2:1, v/v) as an eluent to give **15** as a colorless foam (0.871 g, 0.52 mmol, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35−7.18 (m, 45H, CH_2Ph), 6.32−6.29 (m, α-H-1), 5.86−5.72 (m, 2H, α-H-1:CHOP), 5.58−5.47 (m, β-H-1), 4.98−3.38 (m, 42H, CH_2Ph, H-2, H-3, H-4, H-5, H-6, POCH_3), 2.14, 2.07, 2.06, 2.03, 2.02

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(s, 3H, OCOCH_3), 0.86−0.79 (m, 9H, SiC(CH_3)$_3$), 0.00 to −0.07 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.0 (OCOCH$_3$), 138.7, 138.6, 138.4, 138.3, 138.2, 138.0, 137.9, 137.7, 137.2 (C, Ar), 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 127.3, 127.1, 126.8, 126.7 (CH, Ar), 94.7, 94.2, 94.0 (C-1), 93.5 (β-COCOCH$_3$), 89.4 (α-COCOCH$_3$), 82.5 (CH), 80.7 (CH), 80.5 (CH), 79.8 (CH), 79.5 (CH), 79.2 (CH), 79.1 (CH), 78.7 (CH), 78.6 (CH), 77.2 (CH), 74.9, 74.6, 73.8, 73.7, 73.5, 73.4, 73.3, 73.2, 73.0, 72.7 (CH, CH$_2$), 72.2 (CH), 71.7 (CH), 70.0 (CH), 69.8 (CH), 68.5 (CH$_2$), 68.1 (CH$_2$), 67.8 (CH$_2$), 54.1 (POCH$_3$), 25.9 (SiC(CH_3)$_3$), 21.0, 20.9 (OCOCH_3), 18.0 (SiC(CH$_3$)$_3$), −3.89, −5.14 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 122.7−117.3 (m). HRMS (ESI): calcd for $C_{91}H_{114}B_2O_{21}P_2SiNa$ $[M + Na]^+$ 1677.7175, found 1677.7155.

Boranophosphodiester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (16). Triethylamine (1.13 mL, 8.1 mmol) and benzenethiol (0.850 mL, 8.2 mmol) were added successively to a solution of **13** (0.227 g, 0.20 mmol) in dry THF (2.0 mL), and the mixture was allowed to stir for 16 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and AcOEt (5.0 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with AcOEt (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (98:1:1−97:1:2, v/v/v) as an eluent. The fractions containing **16** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **16** as a colorless foam (0.226 g, 0.19 mmol, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52−7.13 (m, 30H, CH$_2$*Ph*), 6.37, 6.31 (d, J = 3.6 Hz, α-H-1), 6.06−5.91 (m, 1H, α-H-1:C*H*OP), 5.59, 5.53 (d, J = 8.3 Hz, β-H-1), 5.31−3.45 (m, 24H, CH_2Ph, H-2, H-3, H-4, H-5, H-6), 2.61 (q, 6H, NCH_2CH$_3$), 2.09, 2.07, 2.03, 2.01 (s, 3H, OCOCH_3), 0.96 (t, 9H, NCH$_2$CH_3), 0.83−0.79 (m, 9H, SiC(CH_3)$_3$), 0.02 to −0.07 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.5, 169.1 (OCOCH$_3$) 140.2, 140.0, 139.6, 139.3, 139.0, 138.8, 138.4, 138.2, 137.8 (C, Ar), 128.2, 128.0, 127.8, 127.5, 127.3, 127.1, 126.8, 126.6 (CH, Ar), 93.7 (β-COCOCH$_3$), 91.8, 91.2 (C-1), 89.9, 89.6 (α-COCOCH$_3$), 84.0 (CH), 81.1, 81.0, 80.8, 80.5, 80.3, 78.8, 78.5, 77.2, 76.4, 75.9, 75.2, 74.9, 74.4, 74.3, 73.5, 73.2, 73.1, 72.5, 72.4, 72.2, 71.8, 70.5, 70.3, 69.3, 69.1 (CH, CH$_2$), 68.7 (CH$_2$), 44.9 (NCH$_2$CH$_3$), 26.0 (SiC(CH$_3$)$_3$), 21.1 (OCOCH$_3$), 18.1 (SiC(CH$_3$)$_3$), 8.25 (NCH$_2$CH$_3$), −3.79, −5.09 (Si(CH$_3$)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 103.0−93.0 (m). HRMS (ESI): calcd for $C_{62}H_{77}BO_{14}PSi$ $[M - H]^-$ 1115.4919, found 1115.4896.

Boranophosphodiester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (17). Triethylamine (1.33 mL, 9.5 mmol) and benzenethiol (0.983 mL, 9.5 mmol) were added successively to a solution of **15** (0.197 g, 0.12 mmol) in dry THF (1.2 mL), and the mixture was allowed to stir for 6 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and AcOEt (5.0 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with AcOEt (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (98:1:1, v/v/v) as an eluent to give **17** as a colorless foam (0.212 g, 0.11 mmol, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51−7.14 (m, 45H, CH$_2$*Ph*), 6.34−6.27 (m, α-H-1), 6.04−5.85 (m, 2H, α-H-1:C*H*OP), 5.51−5.42 (m, β-H-1), 5.32−3.41 (m, 36H, CH_2Ph, H-2, H-3, H-4, H-5, H-6), 2.55 (q, 12H, NCH_2CH$_3$), 2.03, 2.02, 2.00, 1.99, 1.97, 1.96, 1.89 (s, 3H, OCOCH_3), 0.90 (t, 18H, NCH$_2$CH_3), 0.84−0.75 (m, 9H, SiC(CH^3)^3), 0.00 to −0.08 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 169.0 (OCOCH$_3$), 140.4, 140.1, 139.9, 139.5, 139.2, 139.0, 138.5, 138.1, 137.8 (C, Ar), 128.4, 128.0, 127.8, 127.3, 127.0, 126.6, 126.3 (CH, Ar), 93.6 (β-COCOCH$_3$), 91.9, 91.6, 91.0 (C-1), 89.9, 89.6 (α-COCOCH$_3$), 84.0 (CH), 81.8 (CH), 81.1 (CH), 80.6 (CH), 79.7 (CH), 78.6 (CH), 78.3 (CH), 77.2 (CH), 75.9, 75.6, 75.2, 74.8, 74.2, 73.8, 73.2, 73.0, 72.5, 72.0 (CH, CH$_2$), 71.2 (CH), 70.3 (CH), 70.0 (CH), 69.3 (CH$_2$), 68.6 (CH$_2$), 44.7 NCH$_2$CH$_3$, 25.9 (SiC(CH_3)$_3$), 20.9 (OCOCH_3), 18.0 (SiC(CH$_3$)$_3$), 8.15 NCH$_2$CH$_3$, −3.93, −5.22 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 100.2−92.2 (m). HRMS (ESI): calcd for $C_{95}H_{126}B_2NO_{21}P_2Si$ $[M + H]^+$ 1728.8248, found 1728.8240.

Phosphodiester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (20). Dichloroacetic acid (56 μL) was added to a solution of DMTrOMe (95.8 mg, 0.28 mmol) and compound **16** (0.114 g, 94 μmol) in dry CH_2Cl_2 (1.9 mL) at 0 °C. The mixture was allowed to stir for 1 h at 0 °C. Et_3SiH (0.2 mL) and $CHCl_3$ (5.0 mL) were added successively to the mixture, and the mixture was washed with saturated $NaHCO_3$ aqueous solutions (2 × 7.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (7.0 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the *H*-phosphonate intermediate **18**. A solution of I_2 (47.6 mg, 0.19 mmol) in dry Py (1.78 mL) and H_2O (94 μL) was then added to crude **18**, and the mixture was allowed to stir for 2 h at rt. The mixture was then diluted with $CHCl_3$ (5.0 mL) and washed with a 0.5 M $Na_2S_2O_3$ aqueous solution (5.0 mL) and 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 15 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N (99:1, v/v) as an eluent. The fractions containing **20** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **20** as a yellow oil (0.107 g, 88 μmol, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53−7.16 (m, 30H, CH$_2$*Ph*), 6.34 (d, J = 3.6 Hz, α-H-1), 5.94 (td, 1H, J_{HH} = 3.3 Hz, J_{PH} = 7.7 Hz, α-H-1:C*H*OP), 5.54 (d, J = 8.3 Hz, β-H-1), 5.30−4.99 (m, 2H, CH_2Ph), 4.86−3.45 (m, 22H, CH_2Ph, H-2, H-3, H-4, H-5, H-6), 2.64 (q, 6H, NCH_2CH$_3$), 2.07, 2.03 (s, 3H, OCOCH_3), 1.00 (t, 9H, NCH$_2$CH_3), 0.81−0.79 (m, 9H, SiC(CH_3)$_3$), 0.01 to −0.07 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 169.0 (OCOCH$_3$), 139.8, 139.6, 139.1, 139.0, 138.9, 138.2, 138.1, 137.7 (C, Ar), 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 127.2, 127.0, 126.9, 126.8 (CH, Ar), 93.7 (β-COCOCH$_3$), 92.7 (C-1), 89.8 (α-COCOCH$_3$), 83.9 (CH), 81.0 (CH), 80.6 (CH), 80.5 (CH), 78.2 (CH), 77.2 (CH), 76.0 (CH), 74.8 (CH$_2$Ph), 74.4 (CH$_2$Ph), 74.0 (CH), 73.9 (CH), 73.7 (CH), 73.6 (CH), 73.3, 73.2, 73.1 (CH, CH$_2$), 72.3 (CH), 71.9 (CH$_2$Ph), 70.5 (CH), 70.4 (CH), 69.3 (C-6), 69.2 (C-6), 69.0 (C-6), 44.9 NCH$_2$CH$_3$, 25.9, (SiC(CH$_3$)$_3$), 21.1, 21.0 (OCOCH_3), 18.0 (SiC(CH$_3$)$_3$), 8.22 NCH$_2$CH$_3$, −3.83, −5.14 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −1.54, −1.66 (s). HRMS (ESI): calcd for $C_{68}H_{91}NO_{15}PSi$ $[M + H]^+$ 1220.5890, found 1220.5885.

Phosphodiester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (21). Dichloroacetic acid (62 μL) was added to a solution of DMTrOMe (210 mg, 0.62 mmol) and the compound **17** (0.189 g, 0.10 mmol) in dry CH_2Cl_2 (2.0 mL) at 0 °C. Additional DCA (10 μL) and DMTrOMe (30.7 mg, 90 μmol) were added after 1 h. The mixture was then allowed to stir for 30 min at 0 °C. Et_3SiH (0.9 mL) and $CHCl_3$ (5.0 mL) were added successively to the mixture, and the mixture was washed with saturated $NaHCO_3$ aqueous

solutions (3 × 7.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (7.0 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the *H*-phosphonate intermediate **19**. A solution of I_2 (103 mg, 0.41 mmol) in dry Py−H_2O (2.05 mL, 95:5, v/v) was then added, and the mixture was allowed to stir for 3 h at rt. The mixture was diluted with $CHCl_3$ (5.0 mL) and washed with a 0.5 M $Na_2S_2O_3$ aqueous solution (5.0 mL) and 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 15 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (99:1:0−96:2:2, v/v/v) as an eluent. The fractions containing **21** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **21** as a yellow oil (0.114 g, 62 μmol, 61%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53−7.12 (m, 45H, CH_2Ph), 6.30 (d, *J* = 3.6 Hz, α-H-1), 5.96−5.92 (m, 2H, α-H-1:C*H*OP), 5.45 (d, *J* = 8.0 Hz, β-H-1), 5.32−4.98, (m, 3H, CH_2Ph), 4.89−3.42 (m, 33H, H-2, H-3, H-4, H-5, H-6, CH_2Ph), 2.56 (q, 12H, NCH_2CH$_3$), 1.99 (s, 3H, OOCCH_3) 0.93 (t, 18H, NCH$_2$CH_3) 0.78 (s, 9H, SiC(CH_3)$_3$), −0.02, −0.09 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 169.0 (OCOCH$_3$) 140.1, 140.0, 139.7, 139.2, 139.0, 138.7, 138.5, 138.4, 138.2, 137.8 (C,Ar), 128.1, 127.9, 127.7, 127.5, 127.3, 127.2, 127.0, 126.7, 126.6 (CH, Ar), 93.6 (β-COCOCH$_3$), 92.7, 92.4 (C-1), 89.9 (α-COCOCH$_3$), 83.9 (CH), 81.0 (CH), 80.7 (CH), 80.5 (CH), 80.3 (CH), 79.7 (CH), 78.0 (CH), 77.2 (CH), 75.6 (CH), 74.6, 74.5, 74.2, 73.9, 73.6, 73.0, 72.8, 72.2, 71.9, 71.5, 71.4, 70.4, 70.1 (CH, CH$_2$), 69.1 (CH$_2$), 68.8 (CH$_2$), 44.7 NCH$_2$CH$_3$, 25.9 (SiC(CH$_3$)$_3$), 21.0 (OCOCH$_3$), 18.0 (SiC(CH$_3$)$_3$), 8.21 NCH$_2$CH$_3$, −3.92, −5.23 (Si(CH$_3$)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −1.55, −1.58, −1.65, −1.69 (s). HRMS (ESI): calcd for $C_{95}H_{121}NO_{23}P_2Si$ $[M + 2H]^{2+}$ 1733.7563, found 1733.7544.

Thiophosphodiester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (22). Trifluoroacetic acid (27 μL) was added to a solution of TrOMe (62.9 mg, 0.23 mmol) and the compound **16** (89.3 mg, 73 μmol) in dry CH_2Cl_2 (1.5 mL) at 0 °C. The mixture was allowed to stir for 1 h at 0 °C. Et_3SiH (0.2 mL) and CH_2Cl_2 (5.0 mL) were successively added, and the mixture was washed with saturated $NaHCO_3$ aqueous solutions (2 × 7.0 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (7.0 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the *H*-phosphonate intermediate **18**. The crude **18** was dissolved in dry Py (1.5 mL) and S_8 (12.3 mg, 0.38 mmol) was added at rt. The mixture was allowed to stir for 2.5 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and AcOEt (3.0 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with AcOEt (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (96:1:3, v/v/v) as an eluent. The fractions containing **22** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **22** as a yellow oil (76.9 mg, 62 μmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56−7.14 (m, 30H, CH_2Ph), 6.37, 6.33 (d, *J* = 3.3 Hz, α-H-1), 6.31−6.08 (m, 1H, H-1:C*H*OP), 5.59, 5.55 (d, *J* = 8.0 Hz, β-H-1), 5.47−5.24 (m, 1H, CH_2Ph), 5.07−3.41 (m, 23H, CH_2Ph, H-2, H-3, H-4, H-5, H-6), 2.68 (q, 6H, NCH_2CH$_3$), 2.08, 2.07, 2.06, 2.05, 2.03, 2.00 (s, 3H, OCOCH_3), 0.98 (t, 9H, NCH$_2$CH_3), 0.90−0.78 (m, 9H, SiC(CH_3)$_3$), 0.01 to −0.07 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 169.1 (OCOCH$_3$), 140.3, 140.1, 139.3, 139.2, 139.0, 138.8, 138.4, 138.3, 138.1, 137.7 (C, Ar), 128.5, 128.3, 128.1, 127.8, 127.6, 127.5, 127.3, 127.0, 126.7, 126.6 (CH, Ar), 93.7 (β-COCOCH$_3$), 93.3 (C-1), 89.8 (α-COCOCH$_3$), 83.7 (CH), 81.2 (CH), 80.9 (CH), 80.6 (CH), 80.1 (CH), 78.6 (CH), 77.2 (CH), 76.2, 74.9, 74.8, 74.6, 74.4, 74.2, 73.3, 73.0, 72.6, 72.0, 71.5, 70.4, 70.1, 69.4, 69.2, 68.7 (CH, CH$_2$), 68.6 (CH$_2$), 45.0 NCH$_2$CH$_3$, 26.0, 25.8 (SiC(CH_3)$_3$), 21.0 (OCOCH_3), 18.0 (SiC(CH$_3$)$_3$), 8.25 NCH$_2$CH_3, −3.86, −5.12 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 59.3, 59.2, 56.8, 56.6 (s). HRMS (ESI): calcd for $C_{68}H_{91}NO_{14}PSSi$ $[M + H]^+$ 1236.5662, found 1236.5668.

Phosphodiester-Linked α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (23). $Et_3N \cdot 3HF$ (0.157 mL, 0.97 mmol) was added to a solution of the compound **20** (78.5 mg, 64 μmol) in dry THF (1.2 mL) at 40 °C. The mixture was allowed to stir for 32 h at 40 °C. A 1 M TEAB aqueous solution (5.0 mL) and CH_2Cl_2 (2.0 mL) were added successively to the mixture and the mixture was washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (99:1:0−98:1:1, v/v/v) as an eluent. The fractions containing **23** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **23** as a yellow oil (63.4 mg, 57 μmol, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53−7.17 (m, 30H, CH_2Ph), 6.32 (d, *J* = 3.6 Hz, α-H-1), 5.95−5.90 (m, 1H, α-H-1:C*H*OP), 5.56 (d, *J* = 8.3 Hz, β-H-1), 5.27−4.78 (m, 4H, CH_2Ph), 4.73−3.45 (m, 20H, CH_2Ph, H-2, H-3, H-4, H-5, H-6), 2.60 (q, 6H, NCH_2CH$_3$), 2.08, 2.03 (s, 3H, OCOCH_3), 1.02 (t, 9H, NCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 169.1 (OCOCH$_3$), 139.9, 139.6, 139.1, 139.0, 138.9, 138.3, 138.2, 137.9, 137.7 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.0, 126.9 (CH, Ar), 93.7 (β-COCOCH$_3$), 93.1, 93.0 (C-1), 89.8 (α-COCOCH$_3$), 84.0 (CH), 81.1 (CH), 80.8 (CH), 80.6 (CH), 79.8 (CH), 79.7 (CH), 78.2 (CH), 77.2 (CH), 76.2 (CH), 76.1 (CH), 75.1 (CH$_2$), 74.9 (CH$_2$), 73.9 (CH$_2$), 73.8, 73.7, 73.6, 73.5, 73.2 (CH, CH$_2$), 73.1 (CH$_2$), 72.0 (CH$_2$), 71.2 (CH), 70.8 (CH), 70.4 (CH), 70.0 (CH$_2$), 69.4 (CH$_2$), 45.5 (NCH$_2$CH$_3$), 21.1, 21.0 (OCOCH_3), 9.79 (NCH$_2$CH_3). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −1.85, −1.97 (s). HRMS (ESI): calcd for $C_{56}H_{60}O_{15}P$ $[M - H]^-$ 1003.3675, found 1003.3680.

Phosphodiester-Linked α-D-Glc-(1-*P*-4)-α-D-Glc-(1-*P*-4)-D-Glc-OAc Derivative (24). $Et_3N \cdot 3HF$ (0.16 mL, 0.95 mmol) was added to a solution of the compound **21** (114 mg, 62 μmol) in dry THF (1.2 mL) at 40 °C. The mixture was allowed to stir for 30 h at 40 °C. A 1 M TEAB aqueous solution (5.0 mL) and CH_2Cl_2 (5.0 mL) were added successively to the mixture, and the mixture was washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (98:2:0−96:2:2, v/v/v) as an eluent. The fractions containing **24** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **24** as a colorless foam (87.8 mg, 51 μmol, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53−7.12 (m, 45H, CH_2Ph), 6.30 (d, *J* = 3.6 Hz, α-H-1), 5.94−5.89 (m, 2H, α-H-1:C*H*OP), 5.44 (d, *J* = 8.0 Hz, β-H-1), 5.31−5.07 (m, 2H, CH_2Ph), 4.87−3.36 (m, 34H, CH_2Ph, H-2,

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H-3, H-4, H-5, H-6), 2.58 (q, 12H, NCH_2CH_3), 2.08, 1.99, 1.95 (s, 3H, $OCOCH_3$), 0.94 (t, 18H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.5, 169.0 ($OCOCH_3$), 140.1, 139.9, 139.7, 139.1, 139.0, 138.9, 138.6, 138.5, 138.3, 138.0, 137.8 (C, Ar), 128.2, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.1, 126.9, 126.7 (CH, Ar), 93.6 (β-$COCOCH_3$), 92.9, 92.7 (C-1), 89.9 (α-$COCOCH_3$), 83.9 (CH), 81.1 (CH), 80.6 (CH), 79.7 (CH), 79.5 (CH), 79.4 (CH), 78.1 (CH), 77.2 (CH), 75.0 (CH_2), 74.7 (CH_2), 74.3, 73.9, 73.7, 73.6, 73.5, 73.2, 73.0, 72.9, 72.0, 71.7 (CH, CH_2), 71.1 (CH), 70.7 (CH), 70.5 (CH_2), 70.1 (CH_2), 69.9 (CH_2), 69.1 (CH_2), 44.8 (NCH_2CH_3), 21.0 ($OCOCH_3$), 8.21 (NCH_2CH_3). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −1.73, −1.77, −1.87 (s). HRMS (ESI): calcd for $C_{83}H_{89}O_{23}P_2$ $[M - H]^-$ 1515.5275, found 1515.5271.

Phosphodiester-Linked α-D-Glc-(1-*P*-4)-D-Glc Derivative (25). A 2 M solution of Me_2NH in THF (0.210 mL, 0.42 mmol) was added to a solution of the compound **23** (30.8 mg, 28 μmol) in dry MeCN (0.31 mL) at rt. The mixture was allowed to stir for 4 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and AcOEt (5.0 mL) were added successively to the mixture, and the mixture was washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with AcOEt (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N (99:1, v/v) as an eluent. The fractions containing **25** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **25** as a colorless foam (27.8 mg, 26 μmol, 94%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52−7.14 (m, 30H, CH_2Ph), 5.90 (td, 1H, J_{HH} = 3.0 Hz, J_{PH} = 7.2 Hz, α-H-1:C*H*OP), 5.24−4.47 (m, 13H, α,β-H-1, CH_2Ph), 4.39−3.36 (m, 12H, H-2, H-3, H-4, H-5, H-6), 2.65 (q, 6H, NCH_2CH$_3$), 1.00 (t, 9H, NCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 140.0, 139.9, 138.9, 138.8, 138.6, 138.4, 138.3, 138.1 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.2, 127.1, 126.9, 126.8 (CH, Ar), 97.3 (β-C-1), 93.1 (C-1:COP), 91.0 (α-C-1), 83.9 (CH), 82.9 (CH), 81.2 (CH), 81.1 (CH), 80.8 (CH), 79.7 (CH), 79.3 (CH), 77.2 (CH), 75.2, 75.1, 74.9, 74.8, 74.7, 74.6, 74.5, 74.4 (CH, CH_2), 73.5 (CH_2), 73.3 (CH_2), 73.2 (CH_2), 72.0 (CH_2), 71.9 (CH_2), 71.3 (CH), 71.2 (CH), 70.8 (CH), 70.7 (CH), 70.5 (CH_2), 70.1 (CH_2), 45.0 (NCH_2CH_3), 8.52 (NCH_2CH_3). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −1.75, −1.81 (s). HRMS (ESI): calcd for $C_{54}H_{58}O_{14}P$ $[M - H]^-$ 961.3570, found 961.3591.

Phosphodiester-Linked α-D-Glc-(1-*P*-4)-α-D-Glc-(1-*P*-4)-D-Glc Derivative (26). A 2 M solution of Me_2NH in THF (0.32 mL, 0.64 mmol) was added to a solution of the compound **24** (73.6 mg, 43 μmol) in dry MeCN (0.48 mL) at rt. The mixture was allowed to stir at rt. Additional 2 M solutions of Me_2NH in THF were added after 6 h (0.53 mL, 1.1 mmol) and 36 h (0.43 mL, 0.86 mmol), and the mixture was stirred for another 27 h. A 1 M TEAB aqueous solution (5.0 mL) and $CHCl_3$ (5.0 mL) were then added successively to the mixture, and the mixture was washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (97:2:1−96:2:2, v/v/v) as an eluent. The fractions containing **26** and the *N*,*N*-dimethylaminoglycoside derivative were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was dissolved in an ammonium acetate buffer solution (0.5 mL, pH 4.6) and the solution was allowed to stir for 10 h at rt. The solution was concentrated under reduced pressure. A 1 M TEAB aqueous solution (5.0 mL) and $CHCl_3$ (5.0 mL) were added successively to the residue, and the organic layer was separated. The organic layer was then washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by Sephadex LH-20 (CH_2Cl_2) to give **26** as colorless foam (48.0 mg, 29 μmol, 67%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52−7.13 (m, 45H, CH_2Ph), 5.92−5.89 (m, 2H, α-H-1:C*H*OP), 5.30−3.42 (m, 37H, CH_2Ph, α,β-H-1, H-2, H-3, H-4, H-5, H-6), 2.56 (q, 12H, NCH_2CH$_3$), 0.92 (t, 18H, NCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 140.2, 140.0, 139.2, 139.0, 138.6, 138.4, 138.2, 138.1 (C, Ar), 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0 (CH, Ar), 97.0 (β-C-1), 93.0, 92.7 (C-1:COP), 91.1 (α-C-1), 81.1 (CH), 80.6 (CH), 79.7 (CH), 79.5 (CH), 79.1 (CH), 77.2 (CH), 75.1 (CH_2), 74.6 (CH_2), 73.5 (CH_2), 73.1 (CH_2), 73.0 (CH_2), 72.0 (CH_2), 71.6 (CH_2), 71.1 (CH), 70.6 (CH), 70.5 (CH_2), 70.3 (CH), 69.9 (CH_2), 44.7 (NCH_2CH_3), 8.16 (NCH_2CH_3). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −4.11, −4.37 (s). HRMS (ESI): calcd for $C_{81}H_{88}O_{22}P_2Na$ $[M + Na]^+$ 1497.5135, found 1497.5124.

α-D-Glc-(1-*P*-4)-D-Glc (27). Compound **25** (27.2 mg, 26 μmol) and palladium on activated carbon (10%, 31 mg) in MeOH (2.6 mL) were allowed to stir under atmospheric pressure of H_2 for 11 h. The residue was then filtered through a filter paper and a membrane filter (DISMIC-25JP, 0.50 μm). MeOH−Et_3N (10 mL, 9:1, v/v) was added to the solution and the solvent was removed under reduced pressure. H_2O was added to the residue. The insoluble materials were removed by membrane filtration (DISMIC-13HP, 0.45 μm) to give **27** as a colorless foam (12.0 mg, 23 μmol, 90%). ^1H NMR (D_2O, 300 MHz): δ 5.59−5.56 (m, 1H, α-H-1:C*H*OP), 5.22 (d, J = 3.9 Hz, α-H-1), 4.65 (d, J = 8.0 Hz, β-H-1), 3.98−3.26 (m, 12H, H-2, H-3, H-4, H-5, H-6), 3.19 (q, 6H, NCH_2CH$_3$), 1.27 (t, 9H, NCH$_2$CH_3). ^{13}C NMR (D_2O, 75.5 MHz): δ 98.9 (β-C-1), 98.7, 98.6 (C-1:COP), 94.8 (α-C-1), 77.8, 77.7, 77.6, 76.9, 76.6, 75.6, 74.7, 74.3, 74.2, 73.3, 71.9, 63.3, 63.2, 63.0, 48.8 (NCH_2CH_3), 11.8 (NCH_2CH_3). ^{31}P NMR (D_2O, 121.5 MHz): δ −1.10, −1.13 (s). HRMS (ESI): calcd for $C_{12}H_{23}O_{14}PNa$ $[M + Na]^+$ 445.0718, found 445.0742.

α-D-Glc-(1-*P*-4)-α-D-Glc-(1-*P*-4)-D-Glc (28). The compound **26** (33.6 mg, 20 μmol) and palladium on activated carbon (10%, 30 mg) in MeOH (2.0 mL) were allowed to stir under atmospheric pressure of H_2 for 2 h. The residue was then filtered through a filter paper and a membrane filter (DISMIC-25JP, 0.50 μm). MeOH−Et_3N (10 mL, 9:1, v/v) was added to the solution and the solvent was removed under reduced pressure. H_2O was added to the residue. The insoluble materials were removed by membrane filtration (DISMIC-13HP, 0.45 μm) to give **28** as a colorless foam (14.6 mg, 17 μmol, 84%). ^1H NMR (D_2O, 300 MHz): δ 5.60−5.56 (m, 2H, α-H-1:C*H*OP), 5.22 (d, J = 3.9 Hz, α-H-1), 4.65 (d, J = 8.0 Hz, β-H-1), 4.05−3.27 (m, 18H, H-2, H-3, H-4, H-5, H-6), 3.20 (q, 12H, NCH_2CH$_3$), 1.27 (t, 18H, NCH$_2$CH_3). ^{13}C NMR (D_2O, 75.5 MHz): δ 98.7, 98.6 (β-C-1), 98.3, 98.2 (C-1:COP), 94.7 (α-C-1), 77.8, 77.6, 76.8, 76.7, 76.2, 75.6, 74.8, 74.4, 74.3, 74.1, 71.9, 63.3, 63.2, 63.0, 62.9, 61.6, 49.4 (NCH_2CH_3), 11.0 (NCH_2CH_3). ^{31}P NMR (D_2O, 121.5 MHz): δ −1.12 (s). HRMS (ESI): calcd for $C_{18}H_{34}O_{22}P_2Na$ $[M + Na]^+$ 687.0909, found 687.0922.

2,3,4-Tri-*O*-Bn-α-D-mannopyranosyl Acetate (29). 2,3,4-Tri-*O*-Bn-6-*O*-(4,4′-dimethoxytrityl)-D-mannopyranosyl acetate **S6** (0.182 g, 0.23 mmol) was dissolved in dry CH_2Cl_2 (2.3 mL). Dichloroacetic acid (0.115 mL) was added to the solution at 0 °C. The mixture was allowed to stir for 1 h. Then dry MeOH (5.0 mL) and a saturated $NaHCO_3$ aqueous solution (5.0 mL) were added successively to the mixture. The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (5.0 mL). The organic layers

were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (2:1, v/v) as an eluent to give **29** as a colorless oil (99.0 mg, 0.20 mmol, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40−7.16 (m, 15H, CH_2Ph), 6.14 (d, J = 1.9 Hz, α-H-1), 5.60 (s, β-H-1), 4.97−4.57 (m, 6H, CH_2Ph), 4.09−3.69 (m, 6H, H-2, H-3, H-4, H-5, H-6), 2.07 (s, β-OCOCH_3), 2.02 (s, α-OCOCH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.0 (OCOCH$_3$), 138.1, 138.0, 137.7 (C, Ar), 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6 (CH, Ar), 92.9 (β-C-1), 91.6 (α-C-1), 79.1 (C-3), 75.3 (CH_2Ph), 74.5 (C-2), 73.9 (C-4), 73.5 (C-5), 72.6 (CH_2Ph), 72.2 (CH_2Ph), 61.9 (C-6), 20.9 (OCOCH_3). HRMS (ESI): calcd for $C_{29}H_{32}O_7K$ $[M + K]^+$ 531.1780, found 531.1805.

Boranophosphotriester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-6)-D-Man-OAc Derivative (30). Compounds **10** (0.327 g, 0.45 mmol) and **29** (0.184 g, 0.37 mmol) were dried by repeated coevaporation with dry toluene and dry MeCN and in vacuo overnight. A solution of 1*H*-tetrazole (62.8 mg, 0.90 mmol) in dry MeCN (3.75 mL), which was dried over MS 3A prior to use, was added, and the mixture was allowed to stir for 25 min at rt. A 1 M BH_3·THF solution in THF (1.87 mL, 1.87 mmol) was added and the mixture was allowed to stir for 15 min at rt. A saturated $NaHCO_3$ aqueous solution (5.0 mL) and $CHCl_3$ (5.0 mL) were added successively to the mixture. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solutions (2 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane−AcOEt (5:2, v/v) as an eluent to give **30** as a colorless foam (0.354 g, 0.31 mmol, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.14 (m, 30H, CH_2Ph), 6.20, 6.16 (d, J = 1.9, 1.7 Hz, α-H-1), 5.91−5.85 (m, 1H, α-H-1:C*H*OP), 5.59 (s, β-H-1), 5.03−4.20 (m, 12H, CH_2Ph), 4.01−3.50 (m, 15H, H-2, H-3, H-4, H-5, H-6, POCH_3), 1.99, 1.96 (s, 3H, OCOCH_3), 0.84−0.81 (m, 9H, SiC(CH_3)$_3$), 0.02 to −0.03 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 168.7, 168.6 (OCOCH$_3$), 138.9, 138.1, 137.9, 137.6, 137.5, 137.4 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.9 (CH, Ar), 94.4 (C-1), 91.5 (α-COCOCH$_3$), 80.5 (CH), 79.7 (CH), 79.6 (CH), 79.5 (CH), 79.0 (CH), 78.9 (CH), 75.2 (CH_2), 74.6 (CH_2), 73.7, 73.5, 73.4, 73.3, 73.1, 73.0, 72.6, 72.5, 72.0, 71.9 (CH, CH_2), 69.8 (CH), 69.7 (CH), 68.4 (CH_2), 68.3 (CH_2), 65.7 (CH_2), 65.6 (CH_2), 53.3, 53.2, 53.0, 52.9 (POCH$_3$), 25.9 (SiC(CH_3)$_3$), 20.9 (OCOCH_3), 18.0 (SiC(CH$_3$)$_3$), −3.87, −3.92, −5.10 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 119.7−115.9 (m). HRMS (ESI): calcd for $C_{63}H_{80}BO_{14}PSiNa$ $[M + Na]^+$ 1153.5040, found 1153.5028.

Boranophosphodiester-Linked 4-*O*-TBDMS-α-D-Glc-(1-*P*-6)-D-Man-OAc Derivative (31). Triethylamine (1.75 mL, 12.6 mmol) and benzenethiol (1.30 mL, 12.6 mmol) were added successively to a solution of **30** (0.354 g, 0.31 mmol) in dry THF (3.1 mL), and the mixture was allowed to stir for 17 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and AcOEt (5.0 mL) were added successively to the mixture. The organic layer was separated and washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with AcOEt (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (99:1:0−98:1:1, v/v/v) as an eluent to give **31** as colorless foam (0.369 g, 0.30 mmol, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46−7.16 (m, 30H, CH_2Ph), 6.16−6.14 (m, α-H-1), 6.00−5.95 (m, 1H, α-H-1:C*H*OP), 5.62 (s, β-H-1), 5.09−4.45 (m, 12H, CH_2Ph), 4.31−3.58 (m, 12H, H-2, H-3, H-4, H-5, H-6), 2.79 (q, 6H, NCH_2CH$_3$), 2.08, 2.02, 2.00 (s, 3H, OCOCH_3), 1.13 (t, 9H, NCH$_2$CH_3), 0.92−0.81 (m, 9H, SiC(CH_3)$_3$), 0.02 to −0.04 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.0 (OCOCH$_3$) 139.3, 138.5, 138.2, 137.8, (C, Ar), 128.3, 128.0, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 126.7 (CH, Ar), 92.1, 91.7 (α-COCOCH$_3$), 91.2, 90.9 (C-1), 81.0 (CH), 80.8 (CH), 80.3 (CH), 80.2 (CH), 79.3 (CH), 79.0 (CH), 75.1, 75.0, 74.7, 74.3, 74.2, 74.1, 73.9, 73.7, 73.4, 73.0, 72.6, 72.4, 72.3, 71.8, 71.4 (CH, CH_2), 70.1 (CH), 69.9 (CH), 68.6 (CH_2Ph), 68.5 (CH_2Ph), 62.8 (CH_2Ph), 62.6 (CH_2Ph), 45.0 (NCH_2CH$_3$), 25.9 (SiC(CH_3)$_3$), 21.0 (OOCCH_3), 18.0 (SiC(CH$_3$)$_3$), 8.47 (NCH_2CH$_3$), −3.86, −3.97, −5.16 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 101.2−95.0 (m). HRMS (ESI): calcd for $C_{62}H_{77}BO_{14}PSi$ $[M - H]^-$ 1115.4919, found 1115.4892.

Phosphodiester-Linked 4-*O*-TBDMS-D-Glc-(1-*P*-6)-α-D-Man-OAc Derivative (33). Dichloroacetic acid (0.18 mL) was added to a solution of DMTrOMe (0.307 g, 0.90 mmol) and the compound **31** (0.362 g, 0.30 mmol) in dry CH_2Cl_2 (6.0 mL) at 0 °C. The mixture was allowed to stir for 1 h at 0 °C. Et_3SiH (0.65 mL) and $CHCl_3$ (5.0 mL) were added successively to the mixture and the mixture was washed with saturated $NaHCO_3$ aqueous solutions (2 × 10 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the *H*-phosphonate intermediate **32**. A solution of I_2 (0.152 g, 0.60 mmol) in dry Py−H_2O (6.0 mL, 95:5, v/v) was then added to the crude **32** and the mixture was allowed to stir for 1 h at rt. The mixture was diluted with $CHCl_3$ (5.0 mL) and washed with a 0.5 M $Na_2S_2O_3$ aqueous solution (10 mL) and 1 M TEAB aqueous solutions (2 × 10 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (98:1:1, v/v/v) as an eluent. The fractions containing **33** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **33** containing ca. 8 wt % of triethylammonium dichloroacetate as a yellow oil (0.302 g, 0.25 mmol, 83%, estimated by ^{1}H NMR analysis). The mixture was purified by Sephadex LH-20 (CH_2Cl_2) to give **33** in 14% isolated yield (49.0 mg, 40 μmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.04 (m, 30H, CH_2Ph), 6.13 (d, J = 1.9 Hz, α-H-1), 5.91 (dd, 1H, J_{HH} = 3.0 Hz, J_{PH} = 8.0 Hz, α-H-1:C*H*OP), 5.59 (s, β-H-1), 5.00−4.44 (m, 12H, CH_2Ph), 4.40−3.44 (m, 12H, H-2, H-3, H-4, H-5, H-6), 2.82 (q, 6H, NCH_2CH$_3$), 2.02, 1.99, 1.96 (s, 3H, OCOCH_3), 1.14 (t, 9H, NCH$_2$CH_3), 0.82−0.78 (m, 9H, SiC(CH_3)$_3$), −0.01 to −0.09 (m, 6H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.0 (OCOCH$_3$), 139.4, 138.6, 138.4, 138.3, 138.2, 137.9 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 126.7 (CH, Ar), 92.5, 92.4 (C-1), 91.9 (α-COCOCH$_3$), 80.8 (CH), 80.3 (CH), 80.2 (CH), 79.2 (CH), 77.2 (CH), 75.1 (CH_2Ph), 74.3, 74.0, 73.9 (CH, CH_2), 72.9 (CH_2Ph), 72.4 (CH), 72.3 (CH_2Ph), 71.5 (CH_2Ph), 70.0 (CH), 68.7 (CH_2Ph), 64.3 (CH_2Ph), 45.1 NCH_2CH$_3$, 26.0 (SiC(CH$_3$)$_3$), 21.0 (OCOCH_3), 18.0 (SiC(CH$_3$)$_3$), 8.35 NCH_2CH$_3$, −3.89, −5.11 (Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −3.07 (s). HRMS (ESI): calcd for $C_{62}H_{74}O_{15}PSi$ $[M - H]^-$ 1117.4540, found 1117.4530.

Phosphodiester-Linked α-D-Glc-(1-*P*-6)-D-Man Derivative (34). Et_3N·3HF (0.44 mL, 2.7 mmol) was added to a solution of the compound **33** (0.219 g) containing ca. 4 wt % triethylammonium dichloroacetate in dry THF (3.3 mL) at 40 °C. The mixture was allowed to stir for 44 h at 40 °C. A 1 M TEAB aqueous solution (5.0 mL) and CH_2Cl_2 (2.0 mL) were added successively to the mixture, and the mixture was washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (99:1:0−98:1:1, v/v/v) as an eluent. The fractions containing the desired product were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous

solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give the desired 4-*O*-desilylated α-D-Glc-(1-*P*-6)-D-Man-OAc derivative as a yellow oil (0.136 g, 0.12 mmol, 41% isolated yield from **31**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40−7.20 (m, 30H, CH_2Ph), 6.13 (d, J = 1.9 Hz, α-H-1), 5.91 (dd, 1H, J_{HH} = 3.0 Hz, J_{PH} = 8.0 Hz, α-H-1:C*H*OP), 5.58 (s, β-H-1), 4.94−4.40 (m, 12H, CH_2Ph), 4.29−3.53 (m, 12H, H-2, H-3, H-4, H-5, H-6), 2.80 (q, 6H, NCH_2CH_3), 2.01, 1.99 (s, 3H, $OCOCH_3$), 1.13 (t, 9H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.0 ($OCOCH_3$), 139.0, 138.5, 138.3, 138.2, 137.8 (C, Ar), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2 (CH, Ar), 92.9, 92.8 (C-1), 91.8 (α-$COCOCH_3$), 80.8 (CH), 79.4 (CH), 79.3 (CH), 79.1 (CH), 77.2 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.3 (CH), 74.2 (CH), 74.0 (CH), 73.9 (CH), 73.4 (CH_2), 72.9 (CH_2), 72.3 (CH_2), 71.5 (CH_2), 70.7 (CH), 69.5 (CH_2), 64.2 (CH_2), 64.1 (CH_2), 45.1 NCH_2CH_3, 21.0 ($OCOCH_3$), 8.35 NCH_2CH_3. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −2.78, −3.19 (s). HRMS (ESI): calcd for $C_{56}H_{61}O_{15}PNa$ $[M + Na]^+$ 1027.3640, found 1027.3626. Next, a 2 M solution of Me_2NH in THF (0.65 mL, 1.30 mmol) was added to a solution of the 4-*O*-desilylated α-D-Glc-(1-*P*-6)-D-Man-OAc derivative thus obtained (96.5 mg, 87 μmol) in dry MeCN (0.87 mL) at rt. The mixture was allowed to stir for 3 h at rt. A 1 M TEAB aqueous solution (5.0 mL) and CH_3Cl (5.0 mL) were added successively to the mixture and the mixture was washed with 1 M TEAB aqueous solutions (2 × 5.0 mL). The aqueous layers were combined and back-extracted with CH_3Cl (2 × 5.0 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2−Et_3N−MeOH (99:1:0−98:1:1, v/v/v) as an eluent. The fractions containing **34** were collected and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (5.0 mL) and washed with a 1 M TEAB aqueous solution (5.0 mL). The aqueous layer was back-extracted with $CHCl_3$ (10 mL). The organic layers were combined, filtered through cotton, and concentrated under reduced pressure to give **34** as a colorless foam (80.3 mg, 76 μmol, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.16 (m, 30H, CH_2Ph), 5.84 (dd, 1H, J_{HH} = 3.3 Hz, J_{PH} = 7.4 Hz, α-H-1:C*H*OP), 4.88−4.43 (m, 12H, CH_2Ph), 4.39−3.49 (m, 13H, α,β-H-1, H-2, H-3, H-4, H-5, H-6), 2.69 (q, 6H, NCH_2CH_3), 1.04 (t, 9H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.1, 138.8, 138.7, 138.6, 138.4, 138.2 (C, Ar), 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2 (CH, Ar), 93.0, 92.9 (C-1:COP), 92.1 (C-1), 81.1 (CH), 80.0 (CH), 79.3 (CH), 79.2 (CH), 77.2 (CH), 76.2 (CH), 75.4 (CH), 74.9 (CH_2), 74.7 (CH_2), 73.3 (CH_2), 72.7 (CH_2), 71.8 (CH_2), 70.9 (CH), 70.8 (CH), 70.7 (CH), 69.5 (CH_2), 65.4 (CH_2), 45.2 NCH_2CH_3, 8.34 NCH_2CH_3. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −3.30, −3.50 (s). HRMS (ESI): calcd for $C_{54}H_{59}O_{14}PNa$ $[M + Na]^+$ 985.3535, found 985.3516.

α-D-Glc-(1-*P*-6)-D-Man (35). The compound **34** (28.4 mg, 27 μmol) and palladium on activated carbon (10%, 30 mg) in MeOH (2.7 mL) were allowed to stir under atmospheric pressure of H_2 for 3 h. The residue was filtered through a filter paper and a membrane filter (DISMIC-25JP, 0.50 μm). MeOH−Et_3N (10 mL, 9:1, v/v) was added to the solution. The solvent was removed under reduced pressure. H_2O was added to the residue. The insoluble materials were removed by membrane filtration (DISMIC-13HP, 0.45 μm) to give **35** as a colorless foam (10.3 mg, 20 μmol, 74%). ^{1}H NMR (D_2O, 300 MHz): δ 5.53−5.50 (m, 1H, α-H-1:C*H*OP), 5.17 (d, J = 1.4 Hz, α-H-1), 4.90 (s, β-H-1), 4.22−3.44 (m, 12H, H-2, H-3, H-4, H-5, H-6), 3.19 (q, 6H, NCH_2CH_3), 1.27 (t, 9H, NCH_2CH_3). ^{13}C NMR (D_2O, 75.5 MHz): δ 98.2, 98.1 (C-1:COP), 96.9 (α-C-1), 96.6 (β-C-1), 75.5 (CH), 75.3 (CH), 74.1 (CH), 74.0 (CH), 73.4 (CH), 72.9 (CH), 71.9 (CH), 69.2 (CH), 67.6 (C-6), 63.0 (C-6), 49.4 (NCH_2CH_3), 11.0 (NCH_2CH_3). ^{31}P NMR (D_2O, 121.5 MHz): δ −0.40, −0.46 (s). HRMS (ESI): calcd for $C_{12}H_{23}O_{14}PNa$ $[M + Na]^+$ 445.0718, found 445.0725.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and characterizing data, including ^{1}H, ^{13}C, and ^{31}P spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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